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(54) Title: PROCESS FOR THE SELECTIVE OXIDATION OF ORGANIC COMPOUNDS (57) Abstract A process for oxidizing organic compounds is disclosed. Hydrogen peroxide is used to oxidize an oxidizable organic substrate in the presence of a silica-modified titania/silica-containing catalyst. A method for preparing a catalyst using a copolymer of diethoxysilane and ethyl titanate is also disclosed.		

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TITLE
PROCESS FOR THE SELECTIVE
OXIDATION OF ORGANIC COMPOUNDS

FIELD OF THE INVENTION

5 The invention generally relates to a process for oxidizing organic compounds. In particular, the invention relates to a process utilizing hydrogen peroxide to oxidize an oxidizable organic substrate in the presence of a silica-modified titania/silica-containing catalyst and to a preparation of a catalyst using a copolymer of diethoxysilane and ethyl titanate.

10 BACKGROUND OF THE INVENTION

 Catalytic oxidation processes are important routes to many commercial chemicals. For example, numerous commercial processes for the epoxidation of olefins have been disclosed in the art. One such process involves the reaction of an organic hydroperoxide with an olefin in the presence of catalytic amounts of
15 certain soluble transition metal compounds (e.g., molybdenum, tungsten, or vanadium naphthenates). Some drawbacks to this process include co-production of an alcohol from the hydroperoxide, recovery of the soluble metal catalyst, and the sensitivity of the reaction to water.

 Heterogeneous catalysts which overcome some of the aforesaid problems
20 have also been developed. U.S. Patent No. 3,923,843 claims a process for the epoxidation of an olefinically unsaturated compound comprising reacting the compound in the liquid phase with an organic hydroperoxide in the presence of a catalyst comprising an inorganic siliceous compound in chemical combination with an oxide or hydroxide of titanium. The catalyst is treated with an organic
25 silylating agent before use. In the examples shown, the epoxide selectivity is increased from about 3% to about 15% when comparing the untreated catalyst to the silylated form. The activity for both types of catalyst is about the same.

 Hydrogen peroxide is often employed as an oxidizing agent for the production of organic chemicals. A wide variety of organic compounds may be
30 oxidized utilizing hydrogen peroxide, for example, olefins can be oxidized to epoxides (oxiranes) using this reagent.

 Many titanosilicates have been reported to be useful as oxidation catalysts. For example, the catalytic oxidation of alkanes and alkenes by titanium silicates is disclosed in C. B. Khouw et al., "Studies on the Catalytic Oxidation of Alkanes
35 and Alkenes by Titanium Silicates", Journal of Catalysis 149, 195-205 (1994). Such catalysts are used for the selective oxidation of n-octane using organic hydroperoxides as the oxidants at temperatures below 100°C. The absence of water is deemed critical for catalytic activity.

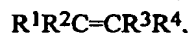
In this regard, there is a need for processes that can utilize aqueous hydrogen peroxide rather than organic hydroperoxides to provide both a safe and an efficient process for oxidizing organic compounds. The present invention satisfies that need and otherwise overcomes certain deficiencies inherent in the prior art. Other objects and advantages of the invention will become apparent to those skilled in the art upon reference to the detailed description which follows hereinafter.

SUMMARY OF THE INVENTION

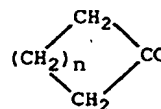
The invention provides a process for oxidizing organic compounds comprising: contacting, in a zone of reaction, an oxidizable organic compound with hydrogen peroxide in the presence of a catalytically effective amount of an insoluble catalyst comprising silicon oxide and an oxide of at least one hydrogen peroxide-activating metal, which catalyst is treated with a silylating agent, and wherein the activity of the treated catalyst is increased by a factor of at least two compared to the untreated catalyst.

Preferably, in the process of the invention, the organic compound is selected from the group consisting of:

(a) cyclic olefins and olefins according to the formula



wherein R^1 , R^2 , R^3 and R^4 are each independently -H; alkyl, wherein the alkyl group has from 1 to 16 carbon atoms; alkylaryl, wherein the alkylaryl group has from 7 to 16 carbon atoms; cycloalkyl, wherein the cycloalkyl group has from 6 to 10 carbon atoms; or alkylcycloalkyl, wherein the alkylcycloalkyl group has from 7 to 16 carbon atoms; and wherein said olefin can optionally containing halogen atoms (i.e., Cl, Br, F, and I);



(b) cyclic ketones according to the formula

wherein n is an integer from 2 to 9;

(c) compounds of the formula $C_6H_5R^5$, wherein R^5 is -H, -OH; C_1 to C_3 straight chain, saturated or unsaturated hydrocarbon radicals, $-CO_2H$; -CN; $-COC_m$, wherein m is an integer from 1 to 6; $-OC_m$, wherein m is an integer from 1 to 6; or NR^6R^7 , where R^6 and R^7 are each independently -H or C_1 to C_3 alkyl groups;

(d) alicyclic hydrocarbons according to the formula $R^8R^9CH_2$,

wherein R^8 and R^9 together form a link of $(-CH_2-)_p$,

wherein p is an integer from 4 to 11;

(e) aliphatic hydrocarbons of the formula C_qH_{2q+2} , wherein q is an integer from 1 to 20; and

(f) alcohols according to the formula $R^{10}R^{11}CHOH$, wherein R^{10} and R^{11} are each independently -H; alkyl, wherein the alkyl group has from 1 to 16 carbon atoms; alkylaryl, wherein the alkylaryl group has from 7 to 16 carbon atoms; cycloalkyl, wherein the cycloalkyl group has from 6 to 10 carbon atoms; cycloalkyl wherein R^{10} and R^{11} taken together form a link containing 4 to 11 $-CH_2-$ groups; or alkylcycloalkyl, wherein the alkylcycloalkyl group has from 7 to 16 carbon atoms.

The invention also provides a process for the preparation of a molecular sieve catalyst comprising synthesizing a catalyst comprising oxides of silicon and titanium by contacting the catalyst with a copolymer of diethoxysilane and ethyl titanate to form a molecular sieve catalyst.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

Hydrogen peroxide-activating metals include, for example, silver, cobalt, cerium, manganese, iron, copper, molybdenum, tungsten, vanadium, titanium, chromium and mixtures thereof. Metallosilicates containing the above metals can be prepared in a similar manner to that described in R. Neumann et al., "Metal Oxide (TiO_2 , MoO_3 , WO_3) Substituted Silicate Xerogels as Catalysts for the Oxidation of Hydrocarbons with Hydrogen Peroxide", Journal of Catalysis, 166, pp. 206-217 (1997).

A presently preferred metal is tetrahedrally coordinated titanium. Metallosilicates which can contain tetrahedrally coordinated titanium include the following molecular sieve structures: silicalite-1 (TS-1), silicalite-2 (TS-2), zeolite-beta, silicon analogs of ZSM-48 and MCM-41. (See R. Murugavel and H. W. Roesky, "Titanosilicates: Recent Developments in Synthesis and Use as Oxidation Catalysts", Angew. Chem. Int. Ed. Engl., 36, No. 5, pp. 477-479 (1997) for a discussion of titanosilicates, their synthesis, and use as oxidation catalysts).

In one embodiment, crystalline titanium silicalite is used as the catalyst. The preparation of porous crystalline titanium silicalite (TS-1) which corresponds to the formula, $xTiO_2(1-x)SiO_2$, where x is between about 0.0005 and about 0.04 has been disclosed in U.S. Patent No. 4,410,501 the contents of which are incorporated herein by reference. TS-1 has been shown to catalyze numerous reactions including the following selective oxidations; aromatic hydroxylations, alkane oxidations and alkene epoxidations. The oxidation reactions are performed using dilute (40% or less) aqueous hydrogen peroxide. The reactions are typically run at 100°C or less and at atmospheric pressure.

Some examples of molecular sieve catalysts prepared by the process of this invention include materials having MFI, MEL, M41S, MOR and BEA type

structures. Materials having an M41S structure are described in A. Corma, Chem. Rev., 97, 2373 to 2419 (1997), particularly at page 2386. The other molecular sieve structures are described in W. M. Meier et al., "Atlas of Zeolite Structure Types", 4th ed., published in Zeolites, 17, Nos. 1/2 (1996).

5 An amorphous titania/silica coprecipitate where the weight ratio of TiO_2 to SiO_2 is between 0.0005:1 and 0.5:1 can also be the catalyst in the above-named oxidation reactions. This material is commercially available or it can be prepared by the procedure disclosed in D. C. M. Dutoit et al., "Titania-Silica Mixed Oxides", Journal of Catalysis, 164, pp. 433-439 (1996).

10 In accordance with this invention, activities are improved by modifying the catalyst with a coating using a silylating agent. Specifically, to improve activity, coating of the oxidation catalyst can be accomplished by a variety of techniques. For example, a sample of the catalyst can be exposed to the ambient atmosphere and immersed in tetraethylorthosilicate (TEOS) for 2 hours; the
15 sample is then filtered and dried at room temperature overnight; (the sample is then heated in flowing nitrogen at 550°C for 3 hours). The preceding treatment can be performed with one or more compounds containing at least one element selected from silicon, aluminum, boron and phosphorus, to deposit substantially, on the external surfaces of the oxidation catalyst, at least 0.05 weight % of the
20 element.

Silicon compounds are the presently preferred coating agents used for silylation. Other suitable silylating agents (besides TEOS) include organosilanes, organosilylamines, and organosilazanes. Examples of suitable silanes include
25 chlorotrimethylsilane $((\text{CH}_3)_3\text{SiCl})$, dichlorodimethylsilane $((\text{CH}_3)_2\text{SiCl}_2)$, bromochlorodimethylsilane $((\text{CH}_3)_2\text{SiBrCl})$, chlorotriethylsilane $((\text{C}_2\text{H}_5)_3\text{SiCl})$ and chlorodimethylphenylsilane $((\text{CH}_3)_2\text{Si}(\text{C}_6\text{H}_5)\text{Cl})$. Examples of suitable silazanes include 1,2-diethylsilazane $(\text{C}_2\text{H}_5)_2\text{SiH}_2\text{NHSiH}_2\text{C}_2\text{H}_5$,
1,1,2,2-tetramethyldisilazane $((\text{CH}_3)_2\text{SiHNHSiH}(\text{CH}_3)_2)$,
1,1,1,2,2,2-hexamethyldisilazane $((\text{CH}_3)_3\text{SiNHSi}(\text{CH}_3)_3)$,
30 1,1,2,2-tetraethyldisilazane $(\text{C}_2\text{H}_5)_2\text{SiHNHSiH}(\text{C}_2\text{H}_5)_2$ and
1,2-diisopropyldisilazane $((\text{CH}_3)_2\text{CHSiH}_2\text{NHSiH}_2\text{CH}(\text{CH}_3)_2)$.

Preferred silylating agents include silazanes and N,O-bis(trimethylsilyl)-trifluoroacetamide $(\text{CF}_3\text{C}(\text{OSi}(\text{CH}_3)_3)=\text{NSi}(\text{CH}_3)_3)$. These two agents do not generate corrosive hydrogen halides when they are used unlike the organosilanes.

35 The silylation of the oxidation catalyst may be done in various ways including that described above. For example, the catalyst particles may be mixed with a liquid silylating agent at temperatures from about room temperature to about 450°C. Alternatively, the catalyst particles may be heated from about 100°C to about 450°C and then contacted with a stream of hot silylating agent

vapor. The silylation may be carried out as a batch, semi-continuous or continuous process.

The time required for the silylating agent to react with the catalyst surface is dependent on the temperature and agent used. Lower temperatures require longer reaction times. Typically, times of from about 0.1 to about 48 hours are suitable.

Although there is no limit to the amount of silylating agent used, for practical reasons it is believed that it can vary from about 1% to about 1000% by weight of the entire catalyst composition. The silylating agent can be applied to the catalyst either in one or a series of treatments.

A wide variety of organic compounds can be oxidized by the process of this invention. Presently preferred organic compounds are listed above in the "Summary of the Invention".

Olefins useful in the process of this invention may be any organic compound having at least one ethylenically unsaturated functional group (i.e., a carbon-carbon double bond) and may be a cyclic, branched, or straight chain olefin. The olefin is reacted with hydrogen peroxide to produce an epoxide (oxirane). The olefin may contain aryl groups such as phenyl. Preferably, the olefin is an aliphatic compound containing from 2 to 20 carbon atoms. Multiple double bonds may be present in the olefin, e.g., dienes, trienes, and other polyunsaturated substrates. The double bond may be in a terminal or internal position of the olefin or may form part of a cyclic structure as in cyclohexene. Other, non-limiting examples of suitable organic compounds include unsaturated fatty acids or esters and oligomeric or polymeric unsaturated compounds such as polybutadiene.

The olefin may optionally contain functional groups such as halide, carboxylic acid, ether, hydroxy, thio, nitro, cyano, ketone, acyl, ester, amino, and anhydride.

Preferred olefins include ethylene, propylene, butenes, butadiene, pentenes, isoprene, and hexenes.

Mixtures of olefins may be epoxidized and the resulting mixtures of epoxides may be used in mixed form or separated into the component epoxides.

Olefins especially preferred for the process of this invention include those of the formula $R^1R^2C=CR^3R^4$, wherein R^1 , R^2 , R^3 and R^4 are each independently selected from the group consisting of H and C_1 to C_{12} straight chain, saturated, or unsaturated hydrocarbon radicals.

Cyclic ketones useful in the process of this invention include cyclopentanone, cyclohexanone. The cyclic ketone is reacted with the in-situ generated hydrogen peroxide to produce lactones. For example, cyclopentanone

is converted to valerolactone and cyclohexanone is converted to caprolactone. Also, in the presence of ammonia cyclohexanone is converted to cyclohexanone oxime.

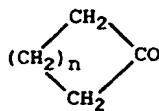
Compounds of the formula $C_6H_5R^5$, wherein R^5 is selected from a group as defined in the "Summary of the Invention", are reacted with hydrogen peroxide to produce phenols. For example, phenol, itself, is converted to hydroquinone and toluene is converted to catechol.

Alicyclic hydrocarbons of the formula $R^8R^9CH_2$, wherein R^8 and R^9 together form a link selected from the group consisting of $(-CH_2-)_p$, wherein p is an integer from 4 to 11 useful in the process of this invention include cyclohexane and cyclododecane. Alicyclic hydrocarbons of the formula $R^8R^9CH_2$ are reacted with hydrogen peroxide to produce ketones and alcohols. For example, cyclohexane is converted to a mixture of cyclohexanol and cyclohexanone and cyclododecane is converted to a mixture of cyclododecanol and cyclododecanone.

Aliphatic hydrocarbons of the formula C_qH_{2q+2} , wherein q is an integer from 1 to 20 useful in the process of this invention include hexane and heptane. Aliphatic hydrocarbons of the formula C_qH_{2q+2} are reacted with hydrogen peroxide to produce alcohols and ketones.

Alcohols according to the formula $R^{10}R^{11}CHOH$, wherein R^{10} and R^{11} are as defined above include 2-butanol, cyclohexanol, and cyclododecanol. These alcohols are oxidized to 2-butanone, cyclohexanone, and cyclododecanone, respectively.

In another embodiment of this invention, oximes can be prepared by



reacting cyclic ketones of the formula , wherein n is an integer

from 2 to 9, with hydrogen peroxide and ammonia in the liquid phase in the presence of the catalysts of this invention and then recovering the oxime product.

The reaction may also be conducted in organic solvents. Some preferred organic solvents are hydrocarbons such as hexane, benzene, methylene chloride, acetonitrile, lower aliphatic alcohols, ketones and dioxane, dimethylformamide and dimethylsulfoxide and mixtures thereof. Preferably, the solvents which are used are ones in which the substrate and products of the reaction are highly soluble.

The reaction is typically conducted at temperatures of from about 0°C to about 200°C , preferably from about 25°C to about 150°C . The reaction pressure is typically from about 1 atmosphere to about 100 atmospheres.

The oxidation products are recovered from the product mixtures by conventional techniques such as fractional distillation, extraction, and crystallization.

- Without further elaboration, it is believed that one skilled in the art can, using the preceding description, utilize the present invention to its fullest extent. The following specific embodiments are, therefore, to be construed as merely illustrative, and are not to limit the remainder of the invention in any way whatsoever. All percentages are by weight unless otherwise indicated.

EXAMPLES

10 Preparation of Catalyst A

Titanium isopropoxide (28.4 g) and isopropyl alcohol (IPA, 30 mL) were mixed and acetylacetone (10.01 g) in IPA (10 mL) was added. The resulting solution was heated to reflux for one hour and then cooled. The IPA was removed under vacuum and the resultant solid was redissolved in IPA to make up 100 mL.

- 15 The solution was 1 molar in Ti.

A portion of the above solution (25.0 mL) was mixed with tetramethylorthosilicate (TMOS, 45.66 mL) and IPA (44 mL). To this was added, dropwise with stirring, a solution of conc. HCl (2.4 mL), H₂O (29.2 g) and IPA (30 mL). This mixture was stirred for 5 min. at room temperature and additional
20 IPA (168 mL) was added. The gel mixture was aged for 64 hours at room temperature with stirring, and thickened slightly.

The sol-gel was extracted with supercritical CO₂ at 40°C at 3500 psig (24.2 MPa) for 5 hours. The resulting fluffy yellow powder was calcined as follows: 400°C for 1 hour in N₂ followed by 600°C for 5 hours in air.

- 25 Catalyst A was x-ray amorphous.

Preparation of Catalyst A2

The procedure for the preparation of Catalyst A was followed except that the gel mixture was aged for 90 hours.

Preparation of Catalyst B

- 30 To Catalyst A (0.508 g) was added a mixture of N,O-bis(trimethylsilyl)-trifluoroacetamide (i.e., CF₃C(OSi(CH₃)₃)=NSi(CH₃)₃ or BSTFA; 1.0 g) and toluene (7.96 g). The mixture was stirred for two hours at room temperature, filtered, the solids washed with toluene, and air dried.

Preparation of Catalyst B2

- 35 To Catalyst A (1.02 g) was added a mixture of 1.05 g BSTFA (1.05 g) and toluene (7.87 g). The slurry mixture was stirred for two hours at room temperature, filtered, the solids washed with toluene, and air dried.

Preparation of Catalyst C

A homogeneous slurry of 50% aqueous NaOH solution (9.066 g), fumed SiO₂ (20 g) and H₂O (98 g) was prepared. The slurry was stirred for 1/2 hour. A solution of dodecyltrimethylammoniumbromide (51.39 g) in H₂O (74.5 g) was added and the mixture was stirred for 1 hour, resulting in a translucent gel. This gel was digested in a Teflon® bottle at 100°C for 5 days. The material was calcined in air as follows: 5°C/min to 250°C; 2°C/min to 550°C; and held at temperature for 4 hours. It was then cooled.

The resultant solid had the x-ray pattern of molecular sieve MCM-41.

The calcined dry MCM-41 (3.5 g) was treated with 0.427 g of TYZOR GBA™ (organic titanate) in toluene (75 mL). While stirring, the treated MCM-41 toluene slurry was heated at reflux overnight, then cooled, filtered, and washed with toluene. The dried material was calcined as follows: 5°C/min to 550°C, held for 4 hours; and cooled.

There was no evidence of anatase or other TiO₂ phases in x-ray diffraction (XRD) or ultraviolet/visible spectral analyses.

Preparation of Catalyst D

To Catalyst C (0.482 g) was added a mixture of BSTFA (1.08 g) and toluene (8.97 g). The slurry mixture was stirred for two hours at room temperature, filtered, the solids washed with toluene, and air dried.

Preparation of Catalyst E

A solution of hexadecyltrimethylammoniumbromide (6.44 g), 25% aqueous tetramethylammoniumhydroxide solution (26.98 g) and H₂O (324.2 g) was prepared. Gelest PSITI-019 (diethoxysilane-ethyltitanate copolymer; 20.0 g) was added dropwise over 15 min. The mixture was stirred for 4 days at room temperature. The filtered, washed, and dried material exhibited the XRD of a mesoporous material, with no TiO₂ phases detectable.

Calcination was as follows: 1°C/min to 550°C; held for 4 hours; and cooled.

Preparation of Catalyst F

To Catalyst E (0.527 g) was added a mixture of BSTFA (1.04 g) and toluene (8.94 g). The mixture was stirred for two hours at room temperature, filtered, the solids washed with toluene, and air dried.

Preparation of Catalyst G

To titanosilicalite (0.123 g; prepared in a manner similar to that described in U.S. Patent No. 4,410,501 and having Ti:SiO₂ weight ratio of 1.9%) was added BSTFA (0.486 g) and toluene (3.96 g). After stirring at room temperature for two hours, the solids were filtered, washed with toluene, and air dried.

EXAMPLE 1Epoxidation of 1-Octene

- To Catalyst B (50 mg) was added 3% aqueous hydrogen peroxide (1.09 g) and 1-octene (2.05 g). The mixture was stirred at room temperature. After 24 hrs, GC analysis showed the presence of 1,2-epoxyoctane in 90% selectivity (18% yield based on peroxide).

EXAMPLE 2Epoxidation of 1-Octene

- To Catalyst B2 (98 mg) was added 3% aqueous hydrogen peroxide (1.03 g) and 1-octene (2.14 g). The mixture was stirred at room temperature. After 24 hrs, GC analysis showed the presence of 1,2-epoxyoctane in 90% selectivity (11% yield based on peroxide).

EXAMPLE 3Epoxidation of cis-Cyclooctene

- To Catalyst B2 (91 mg) was added 10% aqueous hydrogen peroxide (1.05 g) and cis-cyclooctene (2.44 g). The mixture was stirred at room temperature. After 24 hours, GC analysis showed the presence of cyclooctene oxide in 33% yield based on peroxide.

COMPARATIVE EXAMPLE AEpoxidation of 1-Octene

- To Catalyst A (41 mg) was added 3% aqueous hydrogen peroxide (1.02 g) and 1-octene (2.02 g). The mixture was stirred at room temperature. After 24 hrs, GC analysis showed the presence of a trace of 1,2-epoxyoctane (<0.2% yield based on peroxide).

COMPARATIVE EXAMPLE BEpoxidation of 1-Octene

- To Catalyst A2 (118 mg) was added 3% aqueous hydrogen peroxide (1.04 g) and 1-octene (2.11 g). The mixture was stirred at room temperature. After 24 hrs, GC analysis showed the presence of a trace of 1,2-epoxyoctane (<0.6% yield based on peroxide).

COMPARATIVE EXAMPLE CEpoxidation of cis-Cyclooctene

- To Catalyst A2 (100 mg) was added 10% aqueous hydrogen peroxide (1.01 g) and cis-cyclooctene (2.43 g). The mixture was stirred at room temperature. After 24 hours, GC analysis showed no reaction to cyclooctene oxide.

EXAMPLE 4Epoxidation of 1-Octene

To Catalyst D (46 mg) was added 3% aqueous hydrogen peroxide (1.02 g) and 1-octene (2.04 g). The mixture was stirred at room temperature. After 24 hrs, GC analysis showed the presence of 1,2-epoxyoctane in 90% selectivity (22% yield based on peroxide).

COMPARATIVE EXAMPLE DEpoxidation of 1-Octene

To Catalyst C (48 mg) was added 3% aqueous hydrogen peroxide (1.04 g) and 1-octene (2.07 g). The mixture was stirred at room temperature. After 24 hrs, GC analysis showed the presence of a trace of 1,2-epoxyoctane (<0.1% yield based on peroxide).

EXAMPLE 5Epoxidation of 1-Octene

To Catalyst F (53 mg) was added 3% aqueous hydrogen peroxide (1.10 g) and 1-octene (2.11 g). The mixture was stirred at room temperature. After 24 hrs, GC analysis showed the presence of 1,2-epoxyoctane in 90% selectivity (25% yield based on peroxide).

EXAMPLE 6Epoxidation of 1-Octene

To Catalyst G (0.102 g) was added 1-octene (2.11 g) and 1.02 g of 10 wt. % aqueous H₂O₂. After stirring at room temperature for 24 hours, GC analysis showed the presence of 1,2-epoxyoctane in 90% selectivity (23% yield based on peroxide).

EXAMPLE 7Epoxidation of cis-Cyclooctene

To Catalyst G (silylated TS-1) (49 mg) was added 10% aqueous hydrogen peroxide (1.04 g) and cis-cyclooctene (2.21 g). The mixture was stirred at room temperature. After 24 hours, GC analysis showed the presence of cyclooctene oxide in 1% yield based on peroxide.

COMPARATIVE EXAMPLE EEpoxidation of 1-Octene

To Catalyst E (67 mg) was added 3% aqueous hydrogen peroxide (1.04 g) and 1-octene (2.05 g). The mixture was stirred at room temperature. After 24 hrs, GC analysis showed the presence of a trace of 1,2-epoxyoctane (<0.5% yield based on peroxide).

COMPARATIVE EXAMPLE F

Epoxidation of 1-Octene

To 0.101 g of titanosilicalite prepared as Catalyst G above (before silylation) was added 1-octene (2.06 g) and 1.05 g of 10 wt % aqueous H_2O_2 .

- 5 After stirring at room temperature for 24 hours, GC analysis showed the presence of 1,2-epoxyoctane in 90% selectivity (6% yield based on peroxide).

COMPARATIVE EXAMPLE G

Epoxidation of cis-Cyclooctene

- 10 To Catalyst G before silylation (55 mg) was added 10% aqueous hydrogen peroxide (1.08 g) and cis-cyclooctene (2.63 g). The mixture was stirred at room temperature. After 24 hours, GC analysis showed no reaction to cyclooctene oxide.

EXAMPLE 8

- 15 The titanium precursor used in Examples 8 to 10 was Gelest diethoxy-siloxane-ethyltitanate copolymer (# in Gelest catalogue = PSITI-019), $[(C_2H_5O)_2SiO]_x[(C_2H_5O)_2TiO]_y$, 19.1-19.6% Si, 2.1-2.3% Ti. Atomic ratio Si:Ti about 15.

Alkaline Synthesis of Mesoporous SiO_2/TiO_2

- 20 Cetyltrimethylammoniumbromide (6.44 g) was dissolved in tetramethylammoniumhydroxide (26.98 g). The PSITI-019 precursor (20.0 g) was added dropwise with strong agitation. The mixture was stirred at 25°C for 3 days and 17 hours. The products were filtered and washed with distilled H_2O (1 L). The dried white solids were calcined by heating in air at 1°C/min to 550°C, which was maintained for 4 hours before cooling.

- 25 Long range mesoporous order was demonstrated by an XRD peak at 3.2 nm. UV/Visible spectroscopy showed that isolated, as well as oligomeric Ti was present. A very intense band at 960 cm^{-1} in the infrared lends further evidence for framework Ti. The high Ti content in the sample (Si:Ti = 8) was probably the reason for the oligomeric Ti species.

- 30 EXAMPLE 9

Acidic Synthesis of Mesoporous SiO_2/TiO_2

- 35 Cetyltrimethylammoniumbromide (3.22 g) was dissolved in dilute HCl made by combining 36.6 g conc. HCl and 148.5 g H_2O . The PSITI-019 precursor (10.0 g) was added dropwise with strong agitation. The mixture was stirred at 25°C for 3 days and 17 hours. The products were filtered and washed with distilled H_2O (1 L). The dried white solids were calcined by heating in air at 1°C/min to 550°C, which was maintained for 4 hours before cooling.

Long range mesoporous order was demonstrated by an XRD peak at 45 nm. UV/Visible spectroscopy showed that only isolated Ti was present by a single band at 205 nm. A band at 968 cm^{-1} in the infrared lends further evidence for the presence of framework Ti. Elemental analysis showed that Si:Ti = 264.

- 5 This was much higher than was obtained for the alkaline synthesis.

EXAMPLE 10

Synthesis of TS-1

- Tetraethylorthosilicate (15.4 g) was added to the PSITI-019 precursor (4.61 g). 40% aqueous tetrapropylammoniumhydroxide (19.34 g, TPAOH) solution was dripped into the clear alkoxide mixture while stirring vigorously at 25°C. After less than 15 minutes, the mixture gelled into a hard brittle mass. This was broken up and dispersed by the addition of the rest of the TPAOH. Almost all of the solids were dissolved during stirring and addition of H_2O (140.5 g) over a period of about 1 hour. The final clear solution was filtered into a Teflon®
- 10
15
20 bottle, which was sealed and placed into an oven at 100°C. The synthesis was stopped after 5 days and 18 hours. The filtered, washed, and dried material was calcined at 520°C for 10 hours.

- X-ray diffraction analysis showed that a very crystalline MFI structure was obtained. Tetrahedral Ti was present as shown by a single UV/Visible spectral band at 206 nm. The infrared band at 971 cm^{-1} was further evidence of Ti framework incorporation.
- 20

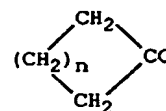
- Although particular embodiments of the present invention have been described in the foregoing description, it will be understood by those skilled in the art that the invention is capable of numerous modifications, substitutions and rearrangements without departing from the spirit or essential attributes of the invention. Reference should be made to the appended claims, rather than to the foregoing specification, as indicating the scope of the invention.
- 25

CLAIMS:

1. A process for oxidizing organic compounds comprising:
 contacting, in a zone of reaction, an oxidizable organic compound
 with hydrogen peroxide in the presence of a catalytically effective amount of an
 insoluble catalyst comprising silicon oxide and an oxide of at least one hydrogen
 peroxide-activating metal, which catalyst has been treated with a silylating agent,
 and wherein the activity of the treated catalyst is increased by a factor of at least
 two compared to untreated catalyst.
2. The process of Claim 1 wherein the organic compound is selected
 from the group consisting of:
 - (a) cyclic olefins and olefins according to the formula

$$R^1R^2C=CR^3R^4,$$

wherein R^1 , R^2 , R^3 and R^4 are each independently -H;
 alkyl, wherein the alkyl group has from 1 to 16 carbon atoms; alkylaryl, wherein
 the alkylaryl group has from 7 to 16 carbon atoms; cycloalkyl, wherein the
 cycloalkyl group has from 6 to 10 carbon atoms; or alkylcycloalkyl, wherein the
 alkylcycloalkyl group has from 7 to 16 carbon atoms; and wherein said olefin can
 optionally containing halogen atoms (i.e., Cl, Br, F, and I);
 - (b) cyclic ketones according to the formula



- wherein n is an integer from 2 to 9;
- (c) compounds of the formula $C_6H_5R^5$, wherein R^5 is -H, -OH; C_1 to C_3 straight chain, saturated or unsaturated hydrocarbon radicals, $-CO_2H$; $-CN$; $-COC_m$, wherein m is an integer from 1 to 6; $-OC_m$, wherein m is an integer from 1 to 6; or NR^6R^7 , where R^6 and R^7 are each independently -H or C_1 to C_3 alkyl groups;
- (d) alicyclic hydrocarbons according to the formula $R^8R^9CH_2$,
 wherein R^8 and R^9 together form a link of $(-CH_2-)_p$,
 wherein p is an integer from 4 to 11;
- (e) aliphatic hydrocarbons of the formula C_qH_{2q+2} , wherein q is an
 integer from 1 to 20; and
- (f) alcohols according to the formula $R^{10}R^{11}CHOH$, wherein R^{10}
 and R^{11} are each independently -H; alkyl, wherein the alkyl group has from 1 to
 16 carbon atoms; alkylaryl, wherein the alkylaryl group has from 7 to 16 carbon
 atoms; cycloalkyl, wherein the cycloalkyl group has from 6 to 10 carbon atoms;
 cycloalkyl wherein R^{10} and R^{11} taken together form a link containing 4 to

11 -CH₂- groups; or alkylcycloalkyl, wherein the alkylcycloalkyl group has from 7 to 16 carbon atoms.

3. The process of Claim 1 wherein the hydrogen peroxide-activating metal is selected from the group consisting of silver, cobalt, cerium, manganese,
5 iron, copper, molybdenum, tungsten, vanadium, titanium, chromium, and mixtures thereof.

4. The process of Claim 1 wherein the hydrogen peroxide-activating metal is tetrahedrally coordinated titanium.

5. The process of Claim 1 wherein the catalyst is crystalline titanium
10 silicalite.

6. The process of Claim 1 where the silylating agent is selected from the group consisting of organosilanes, organosilylamines, and organosilazanes.

7. The process of Claim 1 where the silylating agent is a silazane or N,O-bis(trimethylsilyl)-trifluoroacetamide.

8. The process of Claim 1 where the process is conducted in organic
15 solvents.

9. A process for the preparation of a molecular sieve catalyst comprising synthesizing a catalyst comprising oxides of silicon and titanium by contacting the catalyst with a copolymer of diethoxysilane and ethyl titanate to form a molecular
20 sieve catalyst.

10. The process of Claim 9 wherein the molecular sieve catalyst formed is selected from the group of catalysts having the following designations: MFI, MEL; M41S; MOR; and BEA.

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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<p>(51) International Patent Classification ⁶ : C07D 301/12, C07B 33/00, B01J 31/02, 29/04</p>	<p>A3</p>	<p>(11) International Publication Number: WO 99/26936 (43) International Publication Date: 3 June 1999 (03.06.99)</p>
<p>(21) International Application Number: PCT/US98/24176 (22) International Filing Date: 12 November 1998 (12.11.98) (30) Priority Data: 60/066,429 24 November 1997 (24.11.97) US (71) Applicant (for all designated States except US): E.I. DU PONT DE NEMOURS AND COMPANY [US/US]; 1007 Market Street, Wilmington, DE 19898 (US). (72) Inventors; and (75) Inventors/Applicants (for US only): D'AMORE, Michael, Brian [US/US]; 2406 Granby Road, Wilmington, DE 19810 (US). SCHWARZ, Stephan [DE/US]; 507 Falkirk Road, Wilmington, DE 19803 (US). (74) Agent: SIEGELL, Barbara, C.; E.I. du Pont de Nemours and Company, Legal Patent Record Center, 1007 Market Street, Wilmington, DE 19898 (US).</p>	<p>(81) Designated States: JP, US, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments. (88) Date of publication of the international search report: 2 September 1999 (02.09.99)</p>	
<p>(54) Title: PROCESS FOR THE SELECTIVE OXIDATION OF ORGANIC COMPOUNDS (57) Abstract A process for oxidizing organic compounds is disclosed. Hydrogen peroxide is used to oxidize an oxidizable organic substrate in the presence of a silica-modified titania/silica-containing catalyst. A method for preparing a catalyst using a copolymer of diethoxysilane and ethyl titanate is also disclosed.</p>		

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INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 98/24176

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C07D301/12 C07B33/00 B01J31/02 B01J29/04

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C07D C07B B01J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 937 216 A (CLERICI MARIO G ET AL) 26 June 1990 see column 2; examples 7-13 ---	1-8
Y	US 3 923 843 A (WULFF HARALD P) 2 December 1975 cited in the application see the whole document ---	1-8
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☒ Further documents are listed in the continuation of box C.

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Date of the actual completion of the international search

28 May 1999

Date of mailing of the international search report

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INTERNATIONAL SEARCH REPORT

International Application No

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	THANGARAJ A ET AL: "STUDIES ON THE SYNTHESIS OF TITANIUM SILICALITE, TS-1" ZEOLITES, vol. 12, no. 8, November 1992, pages 943-950, XP002073984 see the whole document ---	1-8
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INTERNATIONAL SEARCH REPORT

International application No.
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Box I Observations where certain claims were found unsearchable (Continuation of Item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

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Box II Observations where unity of invention is lacking (Continuation of Item 2 of first sheet)

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see additional sheet

1. ☒ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.

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INTERNATIONAL SEARCH REPORT

International Application No

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